

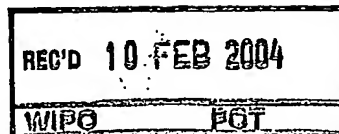


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PCT/CB 2003 / 005663

24 JUN 2005



INVESTOR IN PEOPLE



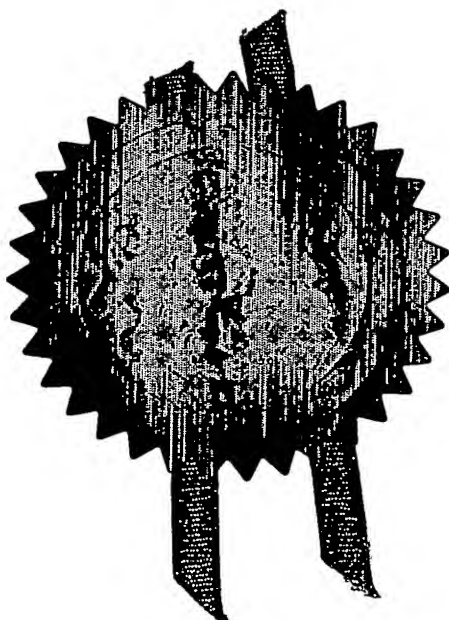
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24 DEC 2002



27DEC02 E7/3486-2 C12133  
P01/7705-0-00-0230074.7

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

24 DEC 2002

The Patent Office

Cardiff Road  
Newport  
South Wales  
NP10 8QQ

1. Your reference

532

2. Patent application number

(The Patent Office will fill in this part)

0230074.7

3. Full name, address and postcode of the or of each applicant (underline all surnames)

ELAM-T LIMITED  
103 BOROUGH ROAD  
LONDON  
SE1 0AA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

810528000

4. Title of the invention

ELECTROLUMINESCENT MATERIALS AND DEVICES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

COHEN, ALAN NICOL  
2 GROVE PLACE  
TATSFIELD  
Nr. WESTERHAM  
KENT  
TN16 2BB

Patents ADP number (if you know it)

6963557001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day / month / year)
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 21

Claim(s) 6

Abstract 1

Drawing(s) 17 + 17 

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature



Date 23/12/02

12. Name and daytime telephone number of person to contact in the United Kingdom

A. N. Cohen

01959 577172

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## Electroluminescent Materials and Devices

The present invention relates to electroluminescent materials and to electroluminescent devices.

5

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used, however these suffer from the disadvantages of high energy consumption, high cost  
10 of manufacture, low quantum efficiency and the inability to make flat panel displays.

Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

15

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

20

Patent application WO98/58037 describes a range of transition metal and lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices

25

using rare earth chelates.

US Patent 5128587 discloses an electroluminescent device which consists of an organometallic complex of rare earth elements of the lanthanide series sandwiched between a transparent electrode of high work function and a second electrode of low

work function with a hole conducting layer interposed between the electroluminescent layer and the transparent high work function electrode and an electron conducting layer interposed between the electroluminescent layer and the electron injecting low work function anode. The hole conducting layer and the  
5 electron conducting layer are required to improve the working and the efficiency of the device. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

10

It is known that electroluminescent europium organometallic complexes emit light in the red part of the spectrum and application WO98/58037 discloses such complexes.

We have now devised an electroluminescent structure which gives improved red  
15 emission.

According to the invention there is provided an electroluminescent device which comprises (i) a first electrode (ii) a layer of a first electroluminescent metal complex or organo metallic complex (iii) a layer of a second metal complex or organo  
20 metallic complex and (iv) a second electrode and in which the band gap of the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the first electroluminescent metal complex or organo metallic complex..

25 There can be more than one layer of each of the first and second electroluminescent metal complex or organo metallic complexes arranged alternatively.

In an electroluminescent organometallic complex when an electron drops from one level to a lower level light is emitted and the larger the gap between the levels (the  
30 band gap) the higher the energy level difference and the shorter the wave length of the light emitted. Normally the metal in the second electroluminescent metal complex or organo metallic complex has a higher HOMO (highest occupied molecular orbital)

and a lower LOMO (lowest occupied molecular orbital) than the metal in the second electroluminescent metal complex or organo metallic complex.

5 The band gap of the second organometallic complex can be larger than the band gap of the first electroluminescent metal complex or organo metallic complex by virtue of the metals and/or organic ligands.

10 The metal in the first and second electroluminescent metal complex or organo metallic complex is preferably selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), U(III), U(VI)O<sub>2</sub>, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III).

15 Alternatively the thickness of the layer of the second electroluminescent metal complex or organo metallic complex is too thin to emit light e.g. of less than 10 nanometres.

20 The metal in the first electroluminescent metal complex or organo metallic complex can be any metal which forms an electroluminescent metal complex or organo metallic complex, provided the band gap is less than the band gap of the organometallic complex in the second metal complex or organo metallic complex.

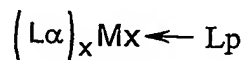
25 Preferred metals in the first electroluminescent metal complex or organo metallic complex are europium which emits light in the red region of the spectrum, terbium which emits light in the green region of the spectrum or dysprosium which emits light in the yellow region of the spectrum.

30 In the present invention the metal in the second electroluminescent metal complex or organo metallic complex is preferably gadolinium which emits light predominately in the ultra violet region of the spectrum. This has the advantage that the ultra violet light emitted has no or a limited effect on the colour of the light emitted by the first electroluminescent metal complex or organo metallic complex another preferred metal is cerium.

The first electroluminescent metal complex or organo metallic complex preferably has the formula  $(L\alpha)_nM1$  where  $L\alpha$  is an organic complex  $M1$  is the metal and  $n$  is the valence state of  $M1$ .

- 5 The second electroluminescent metal complex or organo metallic complex preferably has the formula  $(L\alpha)_mM2$  where  $L\alpha$  is an organic complex  $M2$  is the metal and  $n$  is the valence state of  $M2$ .

10 Preferred electroluminescent compounds which can be used in the present invention are of formula



(A)

- 15 where  $Mx$  is the metal,  $x$  is the valence state of  $Mx$ ;  $L\alpha$  and  $Lp$  are organic ligands and  $Lp$  is a neutral ligand. The ligands  $L\alpha$  can be the same or different and there can be a plurality of ligands  $Lp$  which can be the same or different.

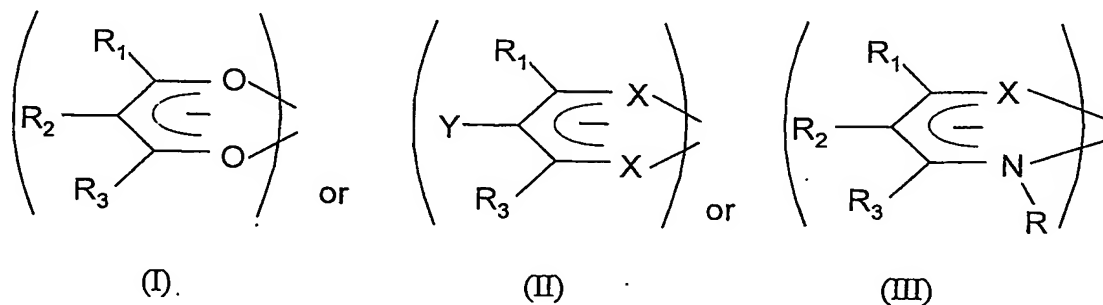
- 20 For example  $(L_1)(L_2)(L_3)Mx (Lp)$  where  $(L_1)(L_2)(L_3)$  are the same or different organic complexes and  $(Lp)$  is a neutral ligand and the different groups  $(L_1)(L_2)(L_3)$  may be the same or different

$Lp$  can be monodentate, bidentate or multidentate and there can be one or more ligands  $Lp$ .

- 25 The metal in the organometallic complex forming the first and second organometallic layers can be the same provided that the organic ligand is such that band gap of the organometallic complex forming the second layer is larger than the band gap of the organometallic complex forming the first organometallic layer.

Further electroluminescent compounds which can be used in the present invention are of general formula  $(L\alpha)_n MxM3$  where M3 is a non rare earth metal,  $L\alpha$  is as above and n is the combined valence state of Eu and M<sub>2</sub>. The complex can also comprise one or more neutral ligands Lp so the complex has the general formula  $(L\alpha)_n MxM3(Lp)$ , where Lp is as above. The metal M3 can be any metal which is not a rare earth, transition metal, lanthanide or an actinide examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

Preferably  $L\alpha$  is selected from  $\beta$  diketones such as those of formulae



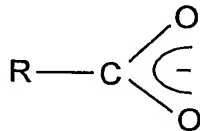
where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring



structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

Examples of  $R_1$  and/or  $R_2$  and/or  $R_3$  include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and unsubstituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

Some of the different groups  $L_\alpha$  may also be the same or different charged groups such as carboxylate groups so that the group  $L_1$  can be as defined above and the groups  $L_2, L_3...$  can be charged groups such as



(IV)

where R is  $R_1$  as defined above or the groups  $L_1, L_2$  can be as defined above and  $L_3...$  etc. are other charged groups.

$R_1, R_2$  and  $R_3$  can also be



where X is O, S, Se or NH.

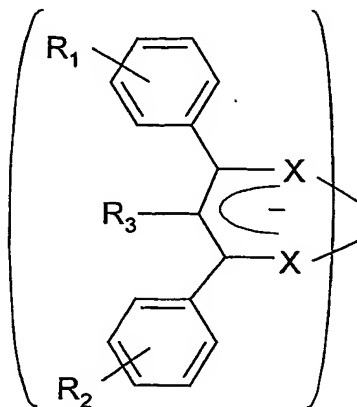
(V)

A preferred moiety  $R_1$  is trifluoromethyl  $CF_3$  and examples of such diketones are, benzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenanthoyltrifluoroacetone, 3-phenanthoyltrifluoroacetone, 9-

anthroyltrifluoroacetone, cinnamoyltrifluoroacetone, and 2-thenoyltrifluoroacetone.

The different groups  $L\alpha$  may be the same or different ligands of formulae

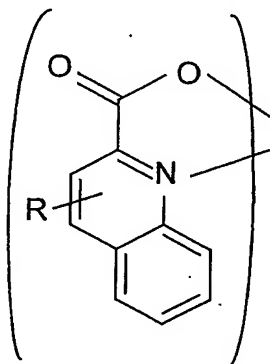
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(VI)

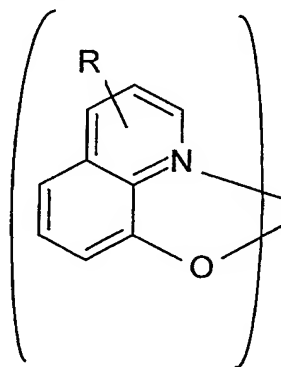
where X is O, S, or Se and  $R_1$ ,  $R_2$  and  $R_3$  are as above

10 The different groups  $L\alpha$  may be the same or different quinolate derivatives such as



(VII)

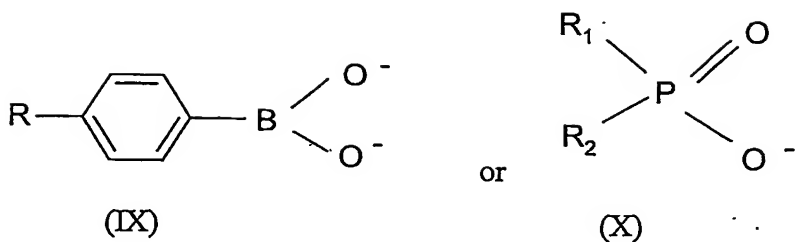
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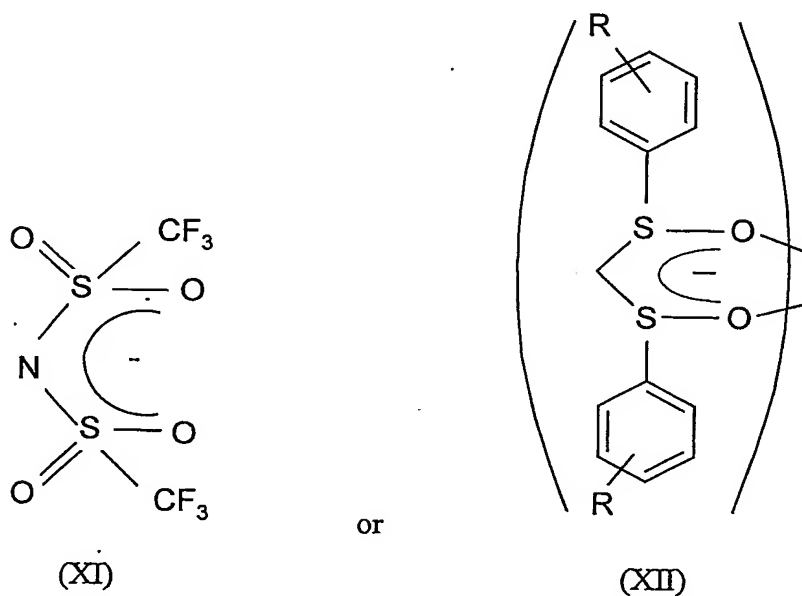
(VIII)

where R is hydrocarbonyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy e.g. the 8 hydroxy quinolate derivatives or

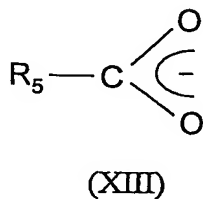
- 8 -



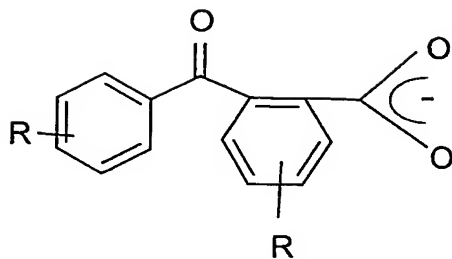
where R, R<sub>1</sub>, and R<sub>2</sub> are as above or are H or F e.g. R<sub>1</sub> and R<sub>2</sub> are alkyl or alkoxy groups



As stated above the different groups L<sub>α</sub> may also be the same or different carboxylate groups e.g.



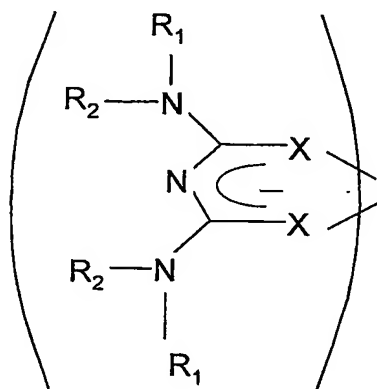
where R<sub>5</sub> is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, R<sub>5</sub> can also be a 2-ethyl hexyl group so L<sub>n</sub> is 2-ethylhexanoate or R<sub>5</sub> can be a chair structure so that L<sub>n</sub> is 2-acetyl cyclohexanoate or L<sub>α</sub> can be



(XIV)

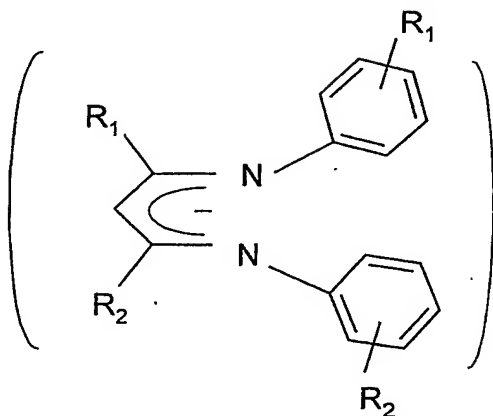
5 where R is as above e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring.

The different groups  $L\alpha$  may also be



(XV)

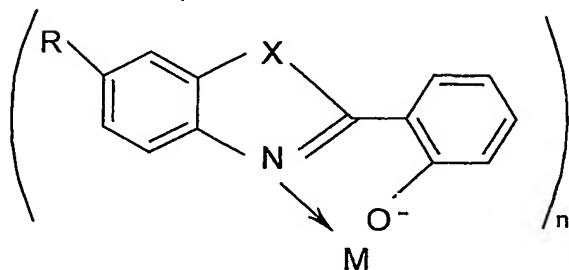
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(XVI)

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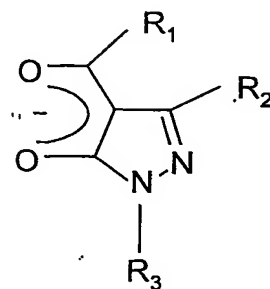
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where X is O, S or Se

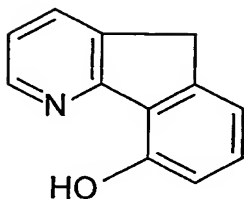
(XVII)

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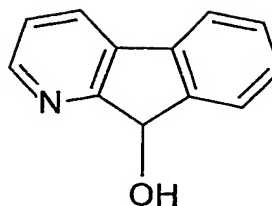
(XVIIa)

Where R, R<sub>1</sub> and R<sub>2</sub> are as above or



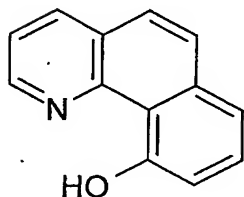
(XVIIb)

or



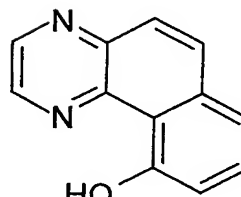
(XVIIc)

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(XVIIId)

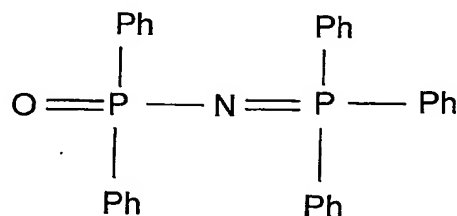
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(XVIIe)

The groups L<sub>p</sub> in the formula (A) above can be selected from

10



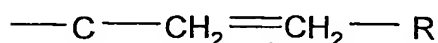
(XVIII)

Where each Ph which can be the same or different and can be a phenyl (OPNP) or a substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polycyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene or pyrene group. The substituents can be for example an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polycyclic group, halogen such as fluorine, cyano, amino. Substituted amino etc. Examples are given in figs. 1 and 2 of the drawings where R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be the same or different and are selected from hydrogen, hydrocarbyl

15

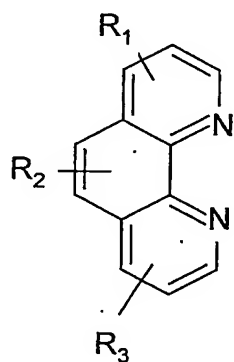
20

- groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups;  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene.  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  can also be unsaturated alkylene groups such as vinyl groups or groups



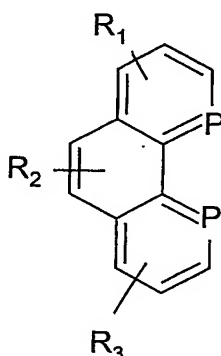
where  $R$  is as above.

- 10  $L_p$  can also be compounds of formulae



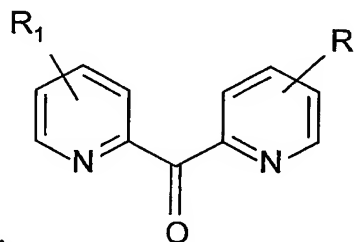
(XVIV)

or



(XX)

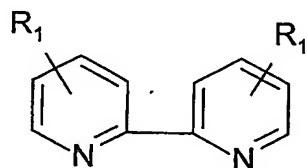
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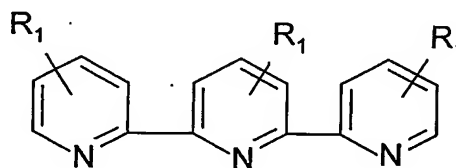
(XXI)

where  $R_1$ ,  $R_2$  and  $R_3$  are as referred to above, for example bathophen shown in fig. 3 of the drawings in which  $R$  is as above or

- 15



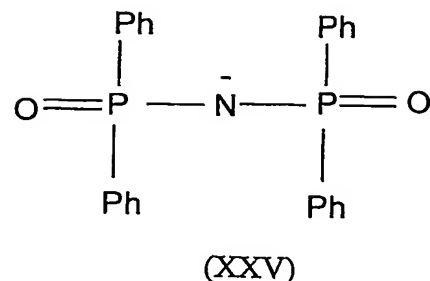
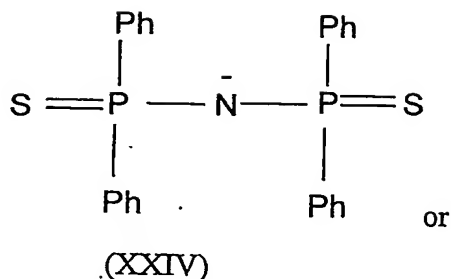
(XXII)



(XXIII)

where  $R_1$ ,  $R_2$  and  $R_3$  are as referred to above.

$L_p$  can also be



5 where Ph is as above.

Other examples of  $L_p$  chelates are as shown in figs. 4 and fluorene and fluorene derivatives e.g. a shown in figs. 5 and compounds of formulae as shown as shown in figs. 6 to 8.

10

Specific examples of  $L_\alpha$  and  $L_p$  are tripyridyl and TMHD, and TMHD complexes,  $\alpha$ ,  $\alpha'$ ,  $\alpha''$  tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA. Where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 11.

15

Preferred first electroluminescent metal complex or organo metallic complexes are  $\text{Eu}(\text{DBM})_3\text{OPNP}$  which has a band gap of 3.2eV and  $\text{Eu}(\text{TMHD})_3\text{OPNP}$  which has a band gap of 3.7 eV and a preferred gadolinium complex is  $\text{Gd}(\text{DBM})_3\text{Phen}$ , where

20

Phen is phenanthrene, which has a band gap of 3.8 eV.

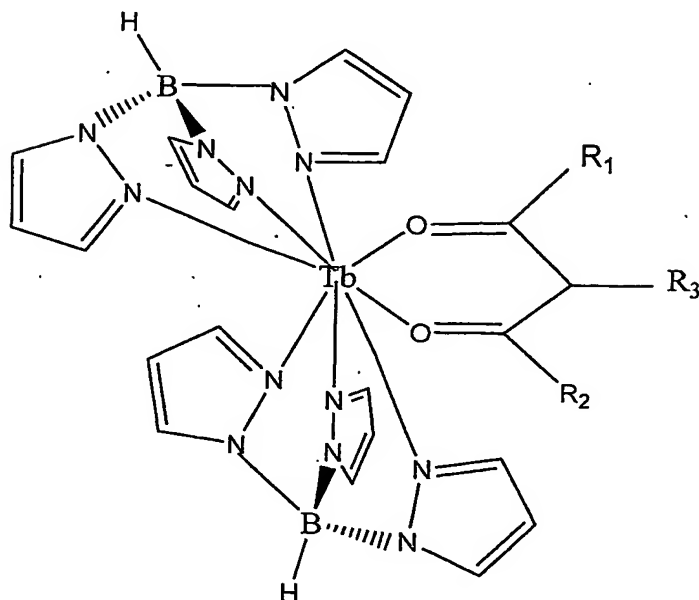
For typical terbium complexes the band gap is of the order of 3.7eV.

In order to increase the conductivity of the second organometallic complex layer the layer can be doped with a conductivity improving additive such as a powdered metal, conductive polymer,

25

Other complexes which can be used to form the second electroluminescent layer are organometallic complexes in which the organic ligand is a boron complex e.g. of formula

5



where  $R_1$  and  $R_2$  are the same or different and are hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups;  $R_1$ ,  $R_2$  and  $R_3$  are the same or different and are hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups;  $R_1$ ,  $R_2$  and  $R_3$  can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures, can be copolymerisable with a monomer e.g. styrene or can be polymer, oligomer or dendrimer substituents.

20 In place of the terbium other lanthanide, actinide or rare earth metal can be used.

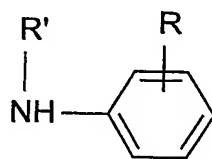


- 5 The first electrode can function as the cathode and the second electrode can function as the anode and preferably there is a layer of a hole transporting material between the anode and the layer of the electroluminescent compound.

10 The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

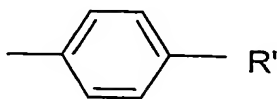
The hole transporting material can be an amine complex such as poly (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted  
15 aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of

20



(XXVI)

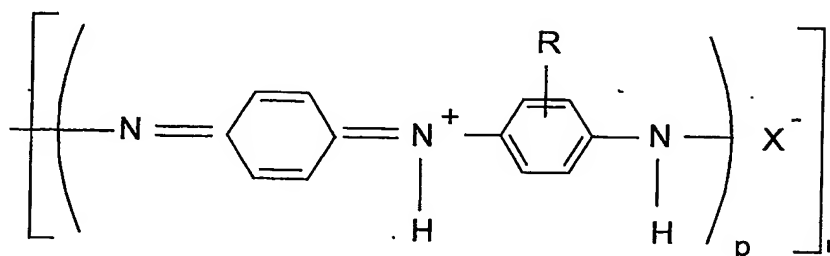
where R is in the ortho - or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



25

where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above.

Or the hole transporting material can be a polyaniline, polyanilines which can be used in the present invention have the general formula



(XXVII)

where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, H<sub>2</sub>PO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate, an example of an arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the unsubstituted or substituted polymer of an amino substituted aromatic compound is deprotonated the it can be easily evaporated i.e. the polymer is evaporable.

Preferably evaporable deprotonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated

unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali such as ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

5

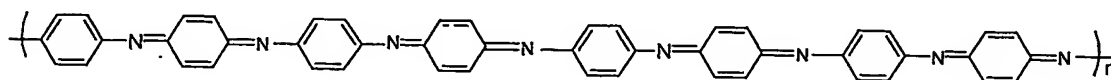
The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

- 10 The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60% e.g. about 50% for example.

Preferably the polymer is substantially fully deprotonated

15

A polyaniline can be formed of octamer units i.e. p is four e.g.



- 20 The polyanilines can have conductivities of the order of  $1 \times 10^{-1}$  Siemen  $\text{cm}^{-1}$  or higher.

The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

- 25 The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic  
5 compound. Polyaminoanthracenes and methods of making them are disclosed in US Patent 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a group R as defined above.

10 Other hole transporting materials are conjugated polymer and the conjugated polymers which can be used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The preferred conjugated polymers are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene  
15 vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group,  
poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes,  
20 polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

In PPV the phenylene ring may optionally carry one or more substituents e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

25

Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthlyene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.

30

The conjugated polymers can be made by the methods disclosed in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The thickness of the hole transporting layer is preferably 20nm to 200nm.

5

The polymers of an amino substituted aromatic compound such as polyanilines referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.

10 The structural formulae of some other hole transporting materials are shown in Figures 12 to 16 of the drawings, where  $R_1$ ,  $R_2$  and  $R_3$  can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups;  $R_1$ ,  $R_2$  and  $R_3$  can  
15 also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or  
20 thiophenyl groups or nitrile.

Examples of  $R_1$  and/or  $R_2$  and/or  $R_3$  include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl,  
25 biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

Optionally there is a layer of an electron injecting material between the cathode and the electroluminescent material layer, the electron injecting material is a material  
30 which will transport electrons when an electric current is passed through electron

injecting materials include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate,  $Mx(DBM)_n$  where  $Mx$  is a metal and DBM is dibenzoyl methane and  $n$  is the valency of  $Mx$  e.g.  $Mx$  is aluminium or chromium. The electron injecting material can also be a cyano anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 9 or 10 of the drawings in which the phenyl rings can be substituted with substituents  $R$  as defined above. Instead of being a separate layer the electron injecting material can be mixed with the electroluminescent material and co-deposited with it.

10

Optionally the hole transporting material can be mixed with the electroluminescent material and co-deposited with it.

15

The hole transporting materials, the electroluminescent material and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

20

The anode is preferably a transparent substrate such as a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer such as a metal or conductive polymer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.

25

The cathode is preferably a low work function metal e.g. aluminium, calcium, lithium, magnesium and alloys thereof such as silver/magnesium alloys, rare earth metal alloys etc., aluminium is a preferred metal. A metal fluoride such as an alkali metal, rare earth metal or their alloys can be used as the second electrode for example by having a metal fluoride layer formed on a metal.

### Device construction

An example of an electroluminescent devices according to the invention are shown in  
figs. 17a, 17b. 17c, 17d of the drawings in which was made by forming sequentially  
5 from solution onto a transparent indium tin oxide glass anode (1) layers in which (2)  
is a hole transporting layer of TPD (3) is a layer of Eu(DBM)<sub>3</sub>OPNP (R1), (4) is a  
layer of Gd(tmhd)<sub>3</sub>Phen (5) is an electron transmitting layer of aluminium quinolate  
(6) is a lithium fluoride layer and (7) is an aluminium cathode.

10 When an electric current is passed through the device red light is emitted via (1).

Various structures were formed and the colour coordinates x;y and their peak  
efficiencies measured and the results shown in the table

Reference	Cd/m <sup>2</sup>	Cd/A	x	y
E8L C1	2.4	1.13	0.66	0.33
E9L b1	15.4	2.01	0.66	0.33
F2J	0.9	3.13	0.66	0.33

15

Where E8L C1 is –

ITO/TPD(35.5nm)/R1(23.6nm)/Gd(tmhd)<sub>3</sub>Phen(20.3nm)/R1(24.2nm)/Alq3(15.5nm)/  
Al

E9L b1 is –

20 ITO/TPD(33nm)/R1(23nm)/Gd(tmhd)<sub>3</sub>Phen(10nm)/R1(10nm)/  
Gd(tmhd)<sub>3</sub>Phen(10nm)/R1(23nm) Alq3(9nm)/Al

F2J is –

ITO/DFDAA(13nm)/ TPD(33nm)/ R1(23nm)/Gd(tmhd)<sub>3</sub>Phen(10nm)/ R1(10nm)/  
Gd(tmhd)<sub>3</sub>Phen(10nm)/R1(23nm) Alq3(9nm)/Al

25

- 21 -

Where DFDAA is a buffer layer.

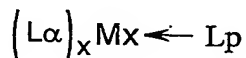


## Claims

1. An electroluminescent device which comprises (i) a first electrode (ii) a layer of a first electroluminescent metal complex or organo metallic complex (iii) a layer of a second metal complex or organo metallic complex and (iv) a second electrode and in which the band gap of the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the first electroluminescent metal complex or organo metallic complex.
2. An electroluminescent device as claimed in claim 1 in which the metal in the first and second electroluminescent metal complex or organo metallic complex is selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), U(III), U(VI)O<sub>2</sub>, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III).
3. An electroluminescent device as claimed in claim 1 in which the metal in the first electroluminescent metal complex or organo metallic complex is europium or terbium and the metal in the second electroluminescent metal complex or organo metallic complex is gadolinium or cerium.
4. An electroluminescent device as claimed in claim 1 or 2 in which the metal in the first electroluminescent metal complex or organo metallic complex and the metal in the second electroluminescent metal complex or organo metallic complex are the same.
5. An electroluminescent device as claimed in any one of claims 1 to 4 in which there are more than one layer of each of the first and second electroluminescent metal complex or organo metallic complexes arranged alternatively.
6. An electroluminescent device as claimed in any one of claims 1 to 5 in which the first electroluminescent metal complex or organo metallic complex has the formula (La)<sub>n</sub>M1 where La is an organic complex M1 is the metal and n is the valence state of M1 and the second electroluminescent metal complex or organo metallic complex

has the formula  $(L\alpha)_n M2$  where  $L\alpha$  is an organic complex  $M2$  is the metal and  $n$  is the valence state of  $M2$ .

7. An electroluminescent device as claimed in any one of claims 1 to 5 in which the metal complex or organo metallic complexes have the formula



(A)

where  $Mx$ ,  $x$ ,  $L\alpha$  and  $Lp$  are as defined herein and the ligands  $L\alpha$  can be the same or different and there can be a plurality of ligands  $Lp$  which can be the same or different.

8. An electroluminescent device as claimed in any one of claims 1 to 4 in which at least one of the metal complex or organo metallic complexes have the formula  $(L\alpha)_n Mx M3$  where  $M3$  is a non rare earth metal,  $L\alpha$  is as defined herein and  $n$  is the combined valence state of  $Mx$  and  $M3$ .

9. An electroluminescent device as claimed in any one of claims 1 to 4 in which at least one of the metal complex or organo metallic complexes have the formula  $(L\alpha)_n Mx M3 (Lp)$ . above.

10. An electroluminescent device as claimed in claim 9 in which the metal  $M3$  is any metal which is not a rare earth, transition metal, lanthanide or an actinide.

11. An electroluminescent device as claimed in claim 9 in which the metal  $M3$  is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium,

cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

- 5      12. An electroluminescent device as claimed in any one of claims 1 to 11 in which  $L\alpha$  is of formula (I) to (XVII) herein.

13. An electroluminescent device as claimed in any one of claims 1 to 11 in which  $Lp$  is of formula (XVIII) to (XXV) herein or figs. 1 to 9 of the drawings

10

14. An electroluminescent device as claimed in any one of claims 1 to 13 in which  $L\alpha$  is selected from tripyridyl and TMHD, and TMHD complexes,  $\alpha$ ,  $\alpha'$ ,  $\alpha''$  tripyridyl and  $Lp$  is selected from crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA.

15

15. An electroluminescent device as claimed in any one of claims 1 to 14 in which the europium complex is  $\text{Eu}(\text{DBM})_3\text{OPNP}$ .

20

16. An electroluminescent device as claimed in any one of claims 1 to 15 in which the gadolinium complex is  $\text{Gd}(\text{DBM})_3\text{Phen}$ .

17. An electroluminescent device as claimed any one of claims 1 to 15 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

25

18. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is an aromatic amine complex.

19. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is polyaromatic amine complex.
20. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is a film of a polymer selected from poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes and substituted polysilanes.
21. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is a film of a compound of formula (XXVI) or (XXVII) herein or as in figures 4 to 8 of the drawings.
22. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is a copolymer of aniline, a copolymer of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with an amino anthracene.
23. An electroluminescent device as claimed in any one of claims 1 to 15 in which the hole transmitting material is a conjugated polymer.
24. An electroluminescent device as claimed in claim 23 in which the conjugated polymer is selected from poly (p-phenylenevinylene)-PPV and copolymers including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes,

polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

5 25. An electroluminescent device as claimed in any one of claims 17 to 24 in which the electroluminescent compound is mixed with the hole transmitting material.

26. An electroluminescent device as claimed in any one of claims 1 to 25 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.

10 27. An electroluminescent device as claimed in claim 26 in which the electron transmitting material is a metal quinolate.

15 28. An electroluminescent device as claimed in claim 25 in which the metal quinolate is an aluminium quinolate or lithium quinolate

29. An electroluminescent device as claimed in claim 26 in which the electron transmitting material is of formula  $Mx(DBM)_n$  where  $Mx$  is a metal and DBM is dibenzoyl methane and  $n$  is the valency of  $Mx$ .

20 30. An electroluminescent device as claimed in claim 26 in which the electron transmitting material is a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate or a compound of formulae shown in figure 2 or 3 of the drawings.

25 31. An electroluminescent device as claimed in any one of claims 26 to 30 in which the electron transmitting material is mixed with the electroluminescent compound.

- 27 -

32. An electroluminescent device as claimed in any one of the claims 1 to 31 in which the first electrode is a transparent electricity conducting glass electrode.
- 5 33. An electroluminescent device as claimed in any one of the claims 1 to 32 in which the second electrode is selected from aluminium, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

- 28 -

### Abstract

5 An improved electroluminescent device has a layer of a first electroluminescent metal complex or organo metallic complex and a layer of a second metal complex or organo metallic complex in which the band gap of the metal in the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the metal in the first electroluminescent metal complex or organo metallic complex..

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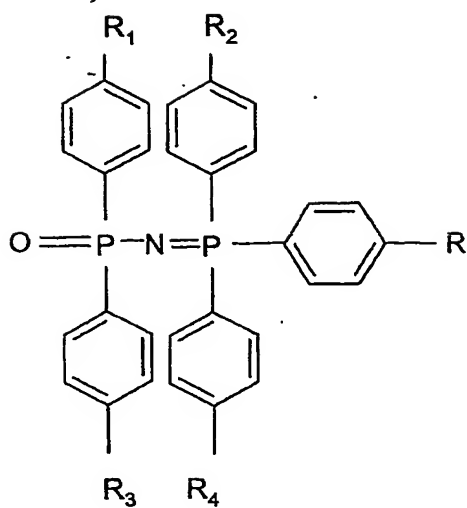


Fig. 1

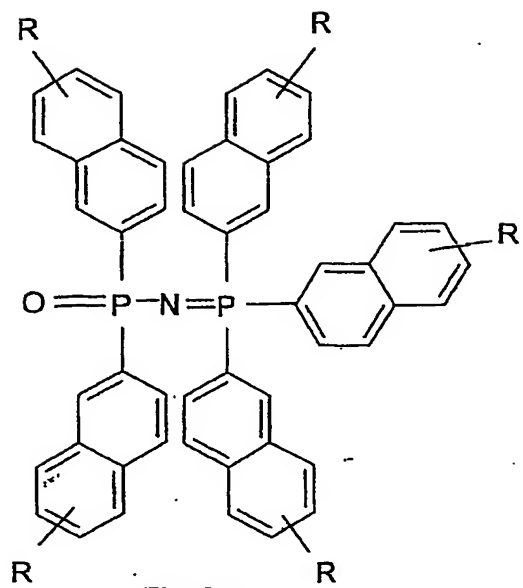


Fig. 2a

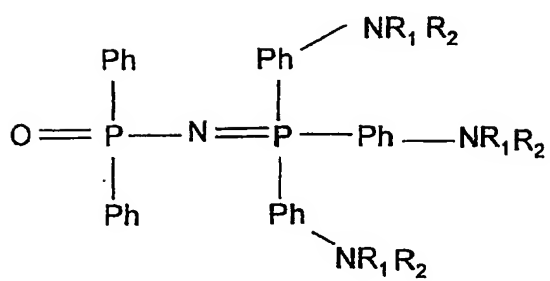


Fig. 2b

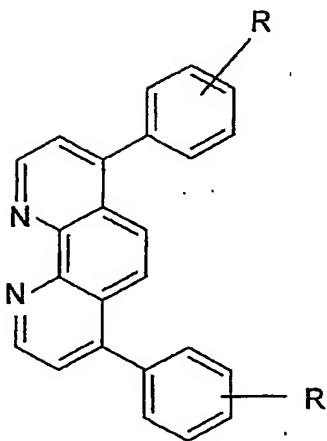


Fig. 3



2/17

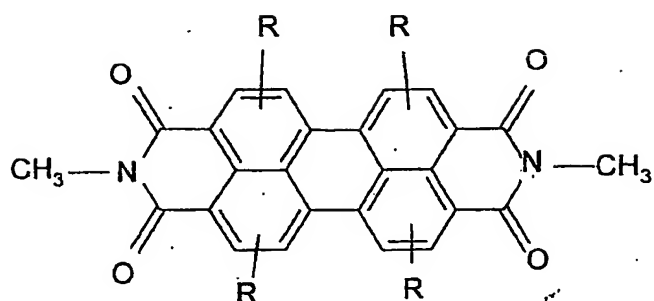


Fig. 4a

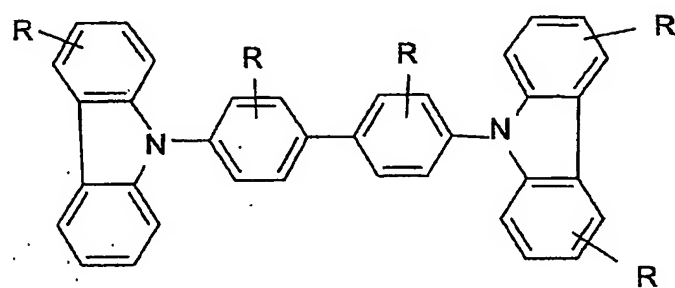


Fig. 4b

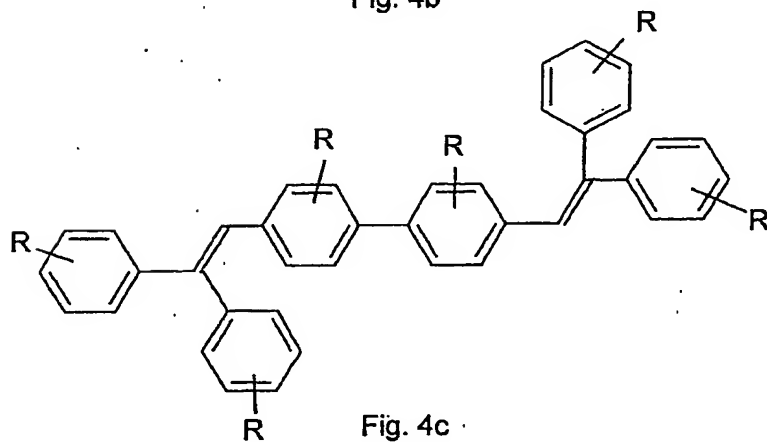


Fig. 4c

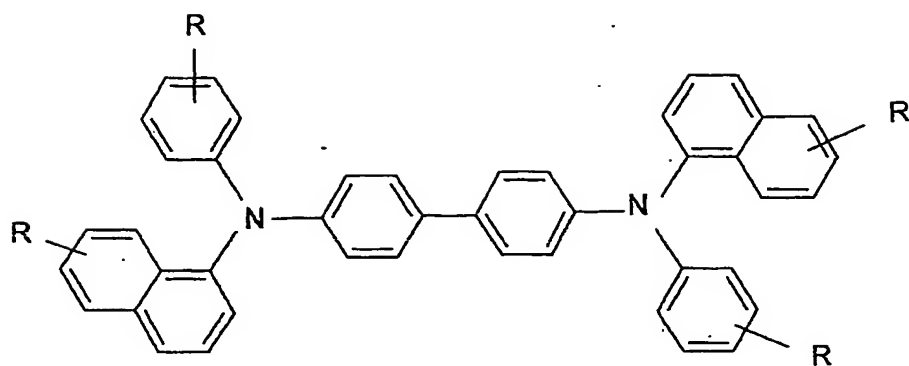


Fig. 4d

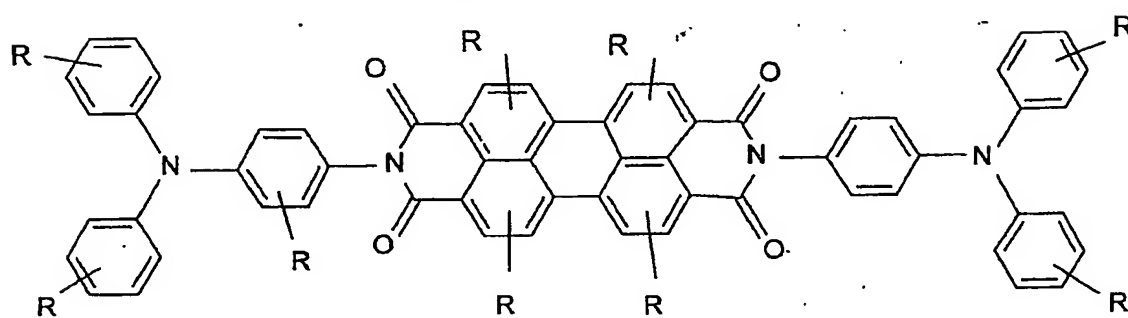


Fig. 4e

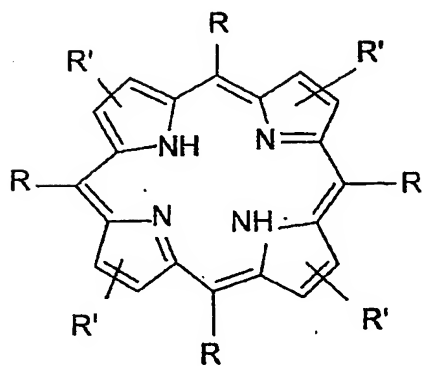


Fig. 4f

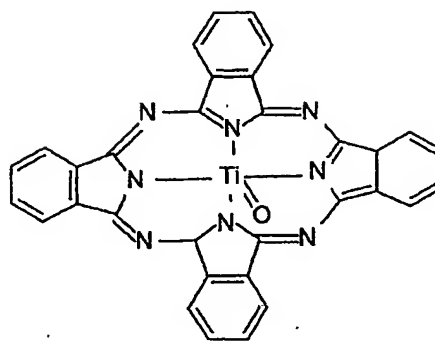


Fig. 4g

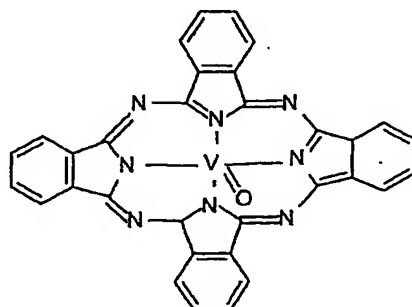


Fig. 4h

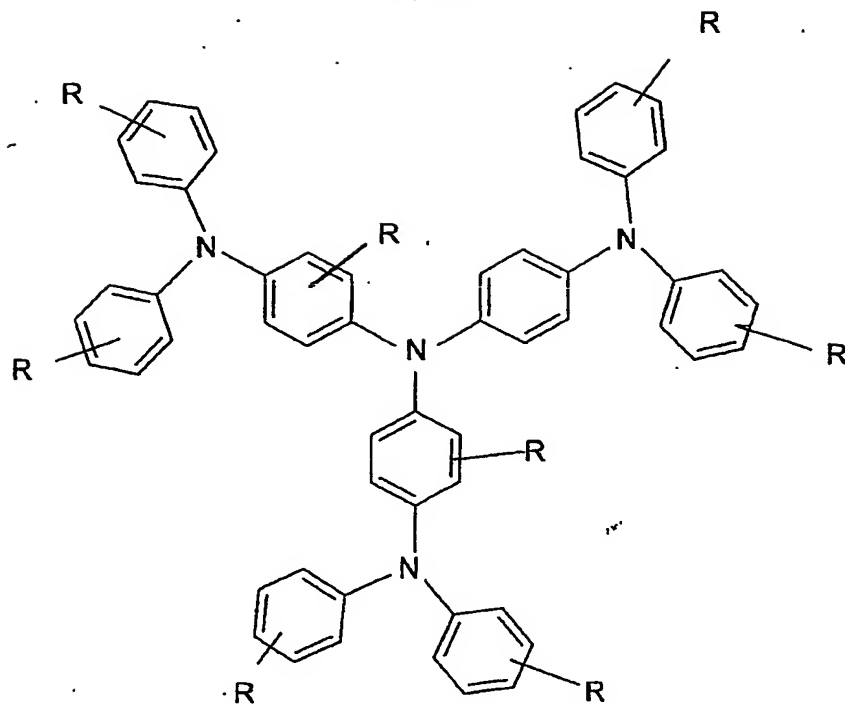


Fig. 4i

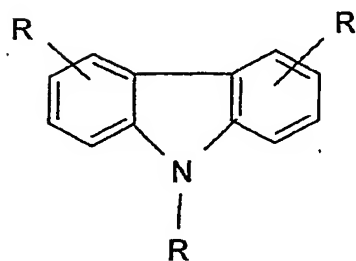


Fig. 4j

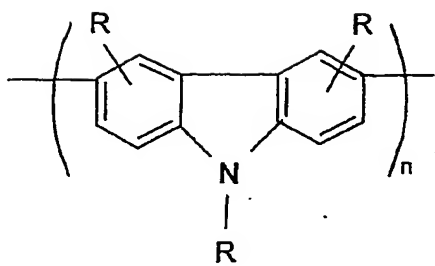


Fig.4k

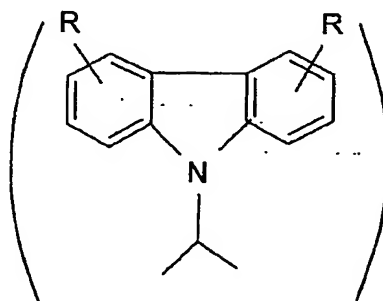


Fig. 4l

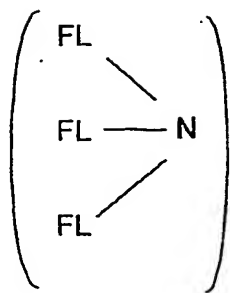


Fig. 5a

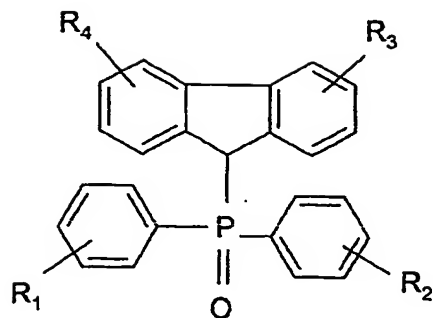


Fig. 5b

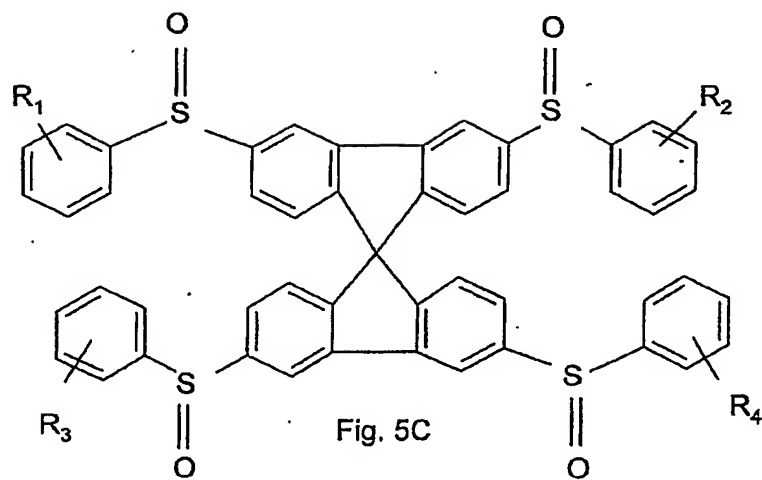


Fig. 5c

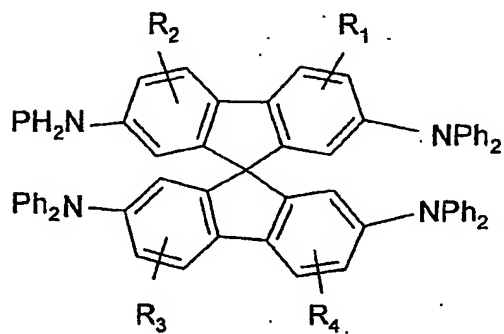


Fig. 5d

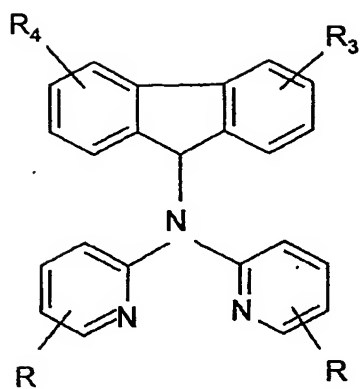


Fig. 5f

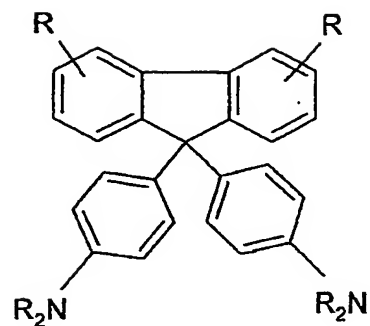


Fig. 5g

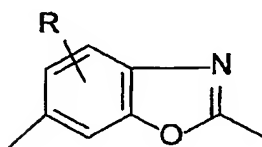


Fig. 6a

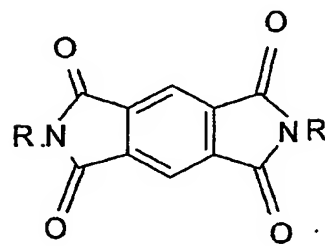


Fig 6b

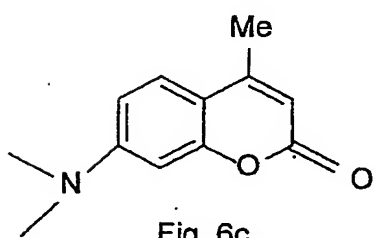


Fig. 6c

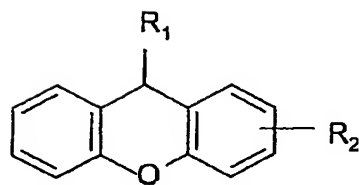


Fig. 6d

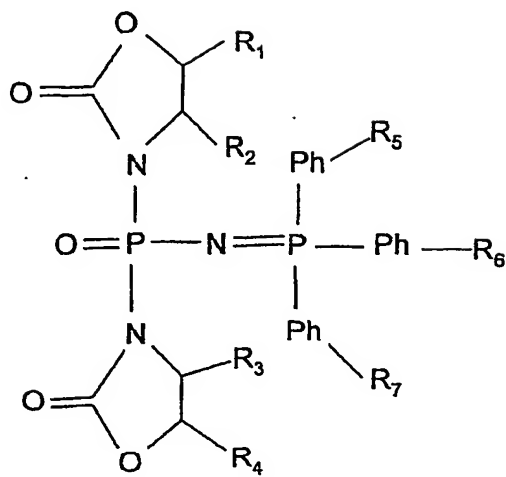


Fig. 6e

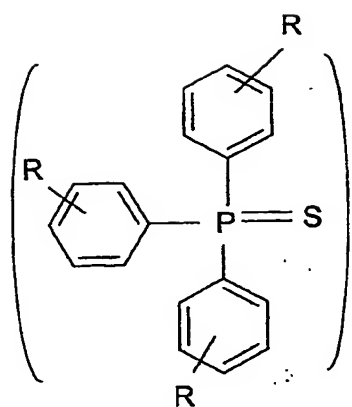


Fig. 7a

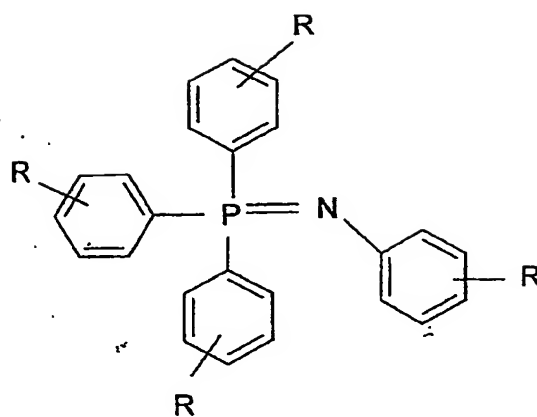


Fig. 7b

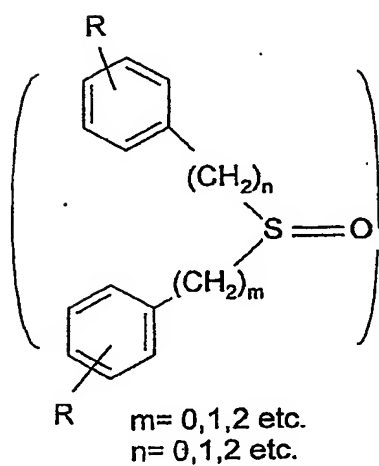


Fig. 7c

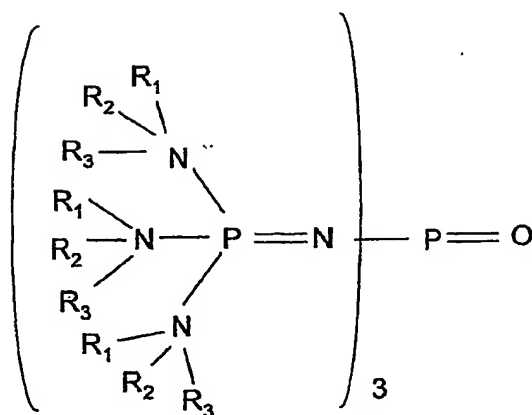


Fig. 7d

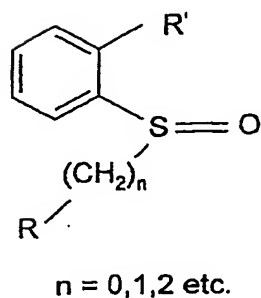


Fig. 7e

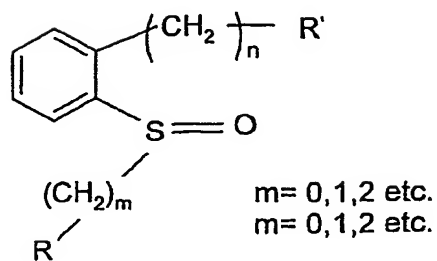


Fig. 7f

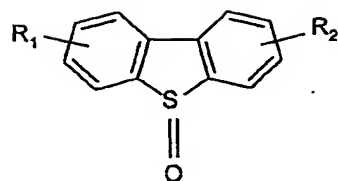


Fig. 8a

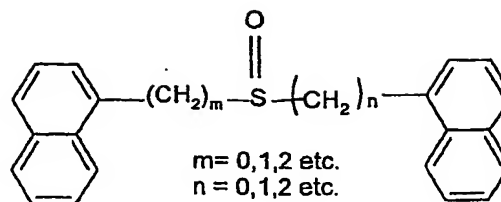


Fig. 8b

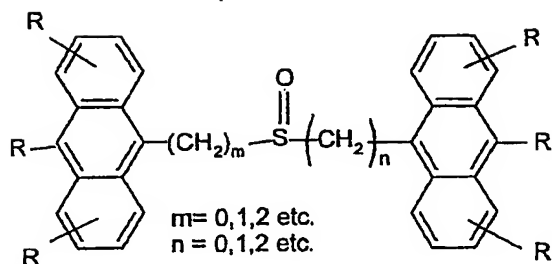


Fig. 8c



Fig. 8d

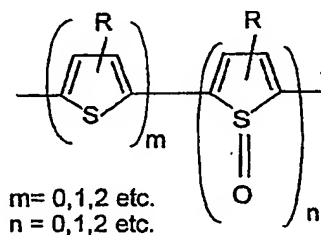


Fig. 8e

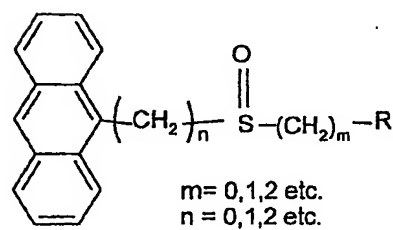


Fig. 8f

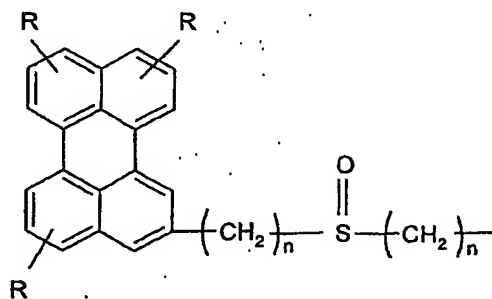


Fig. 8g

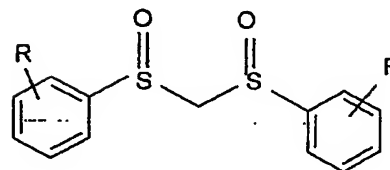
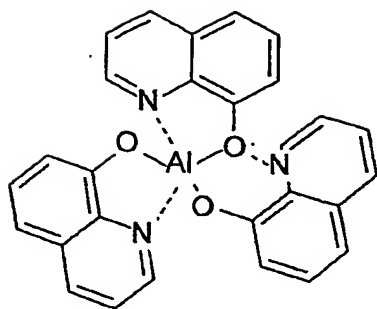
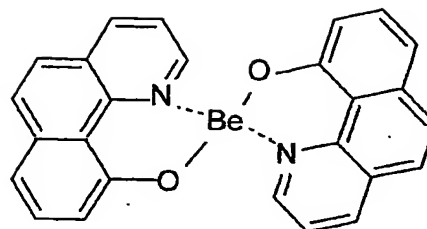


Fig. 8g

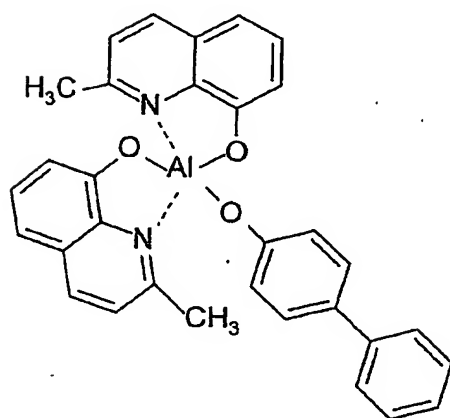
9/17



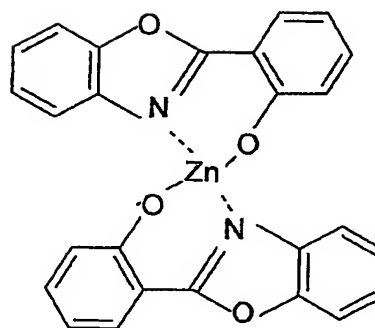
Alq



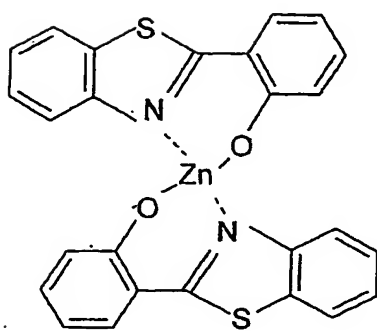
Bebq



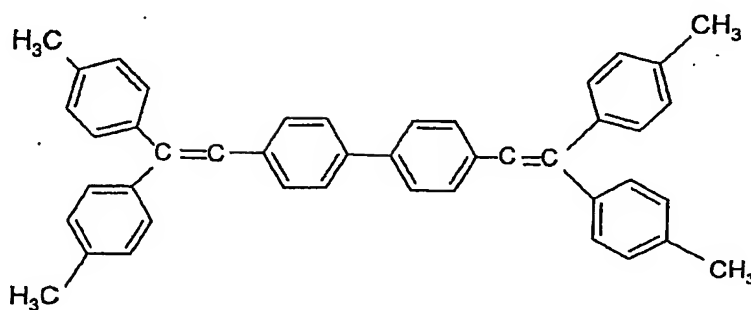
BAiq1



ZnPBO



ZnPBT

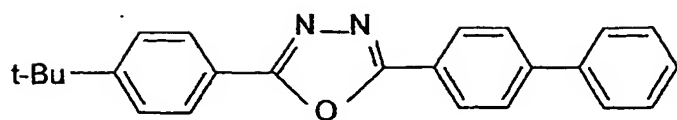


DTVb1

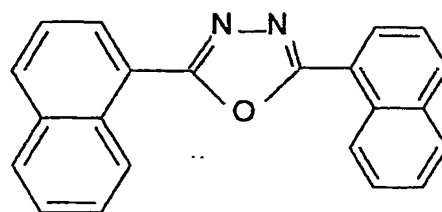
Fig. 9



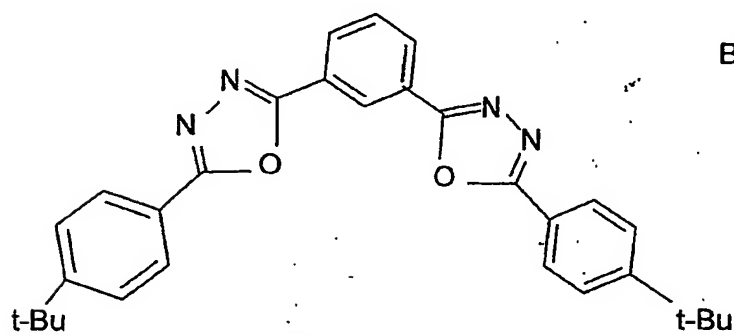
10/17



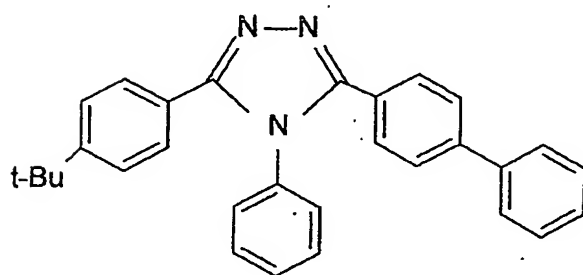
t-Bu-PBD



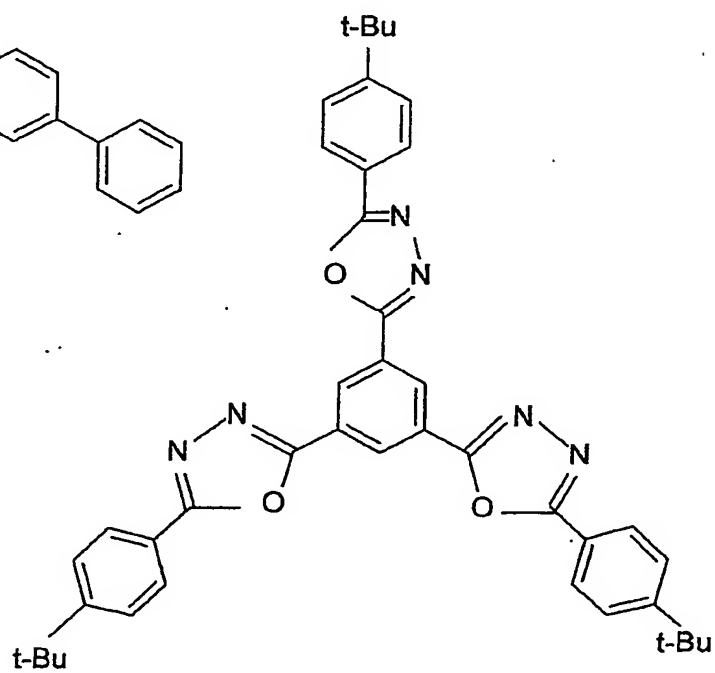
BND



OXD-7



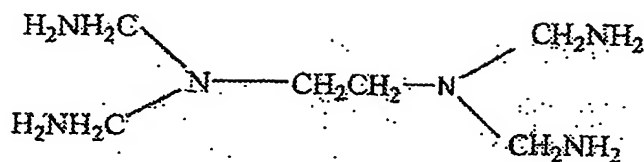
TAZ



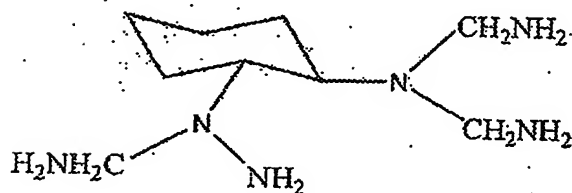
OXD-Star

Fig. 10

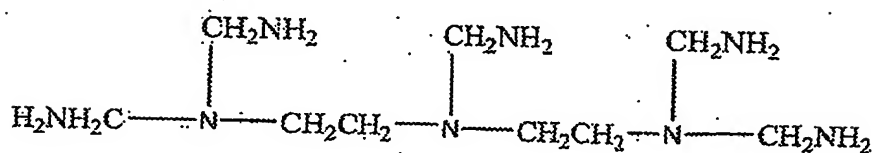
11/17



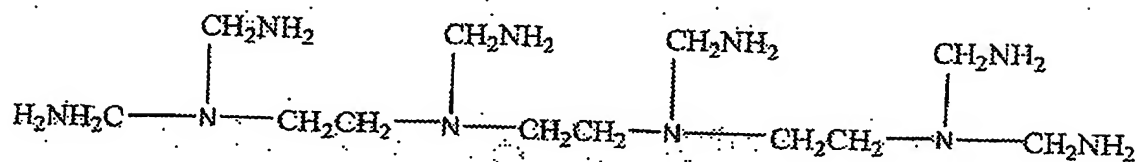
EDTA



DCTA



DTPA



TTHA

Fig. 11

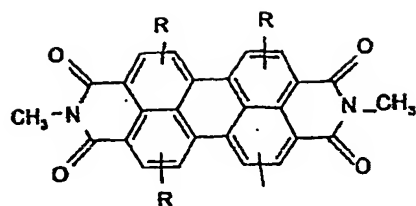


Fig. 12a

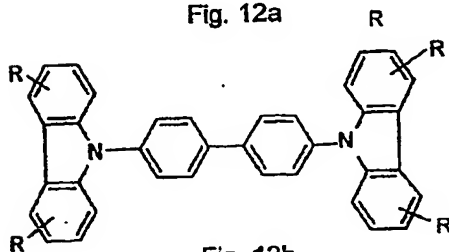


Fig. 12b

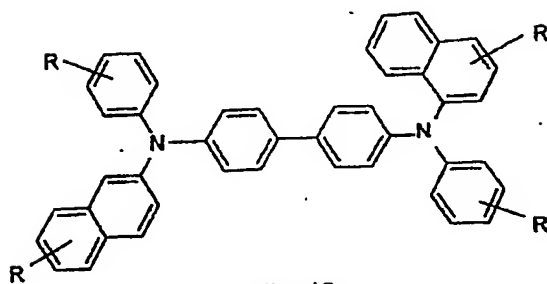


Fig. 12c

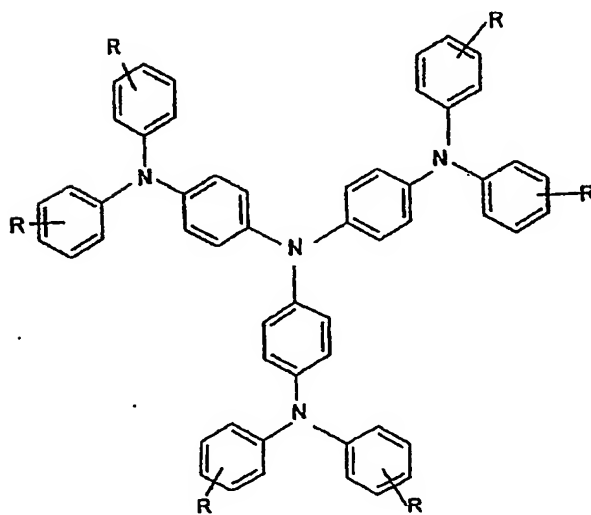


Fig. 12d

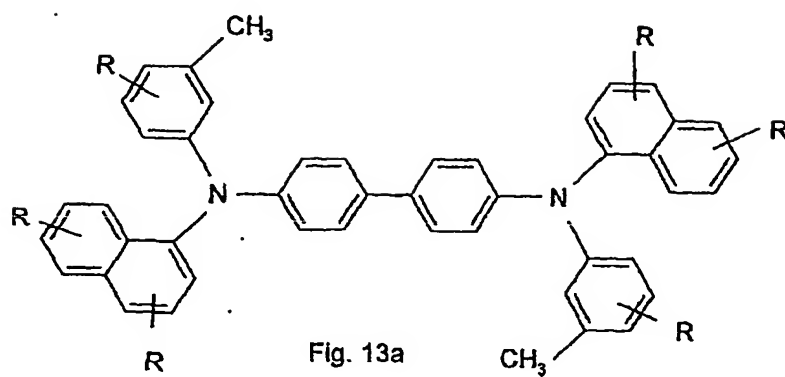


Fig. 13a

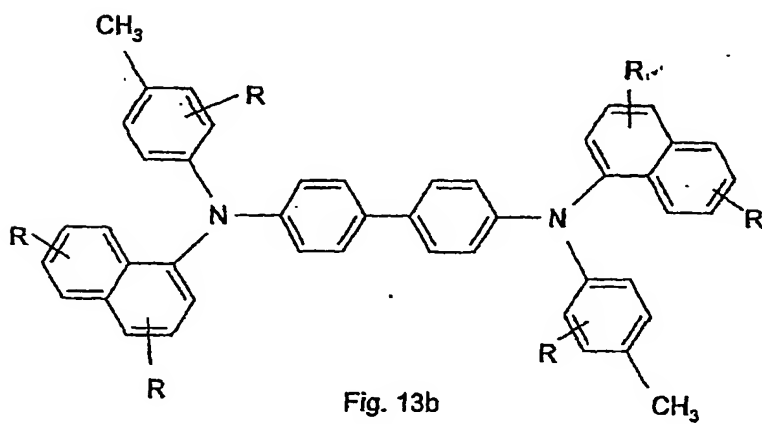


Fig. 13b

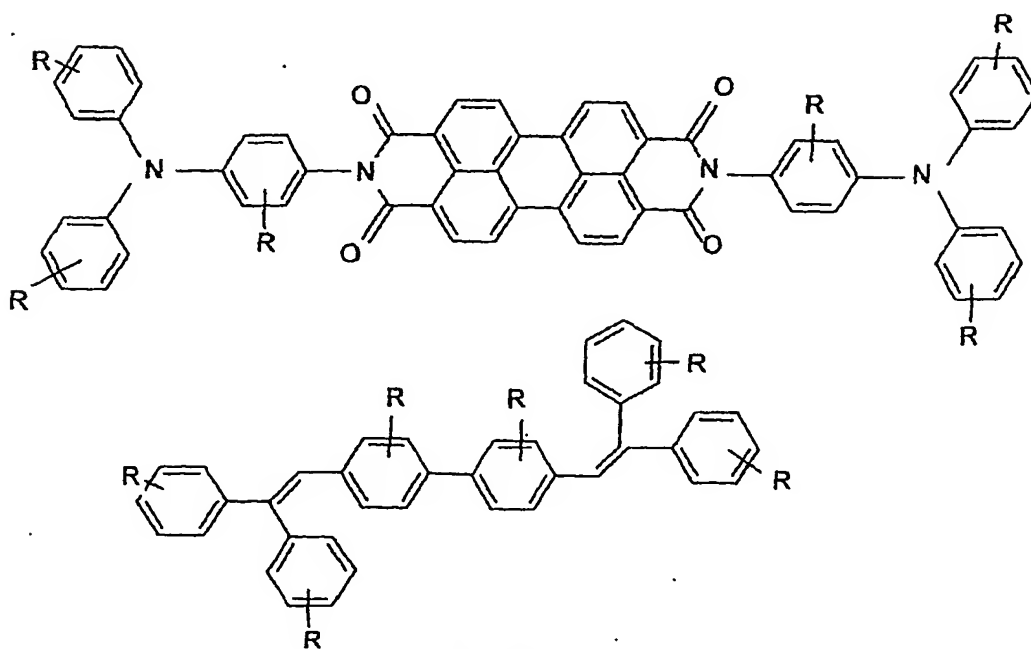


Fig. 13c

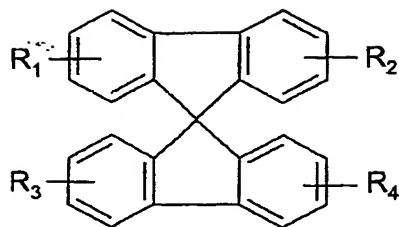


Fig. 14a

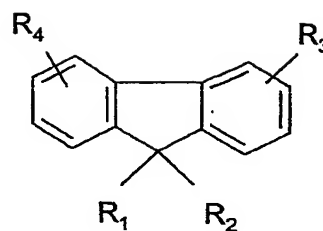
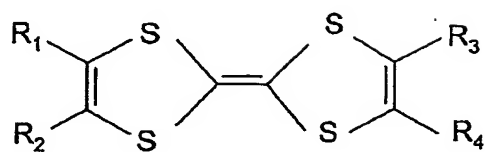


Fig. 14b



or

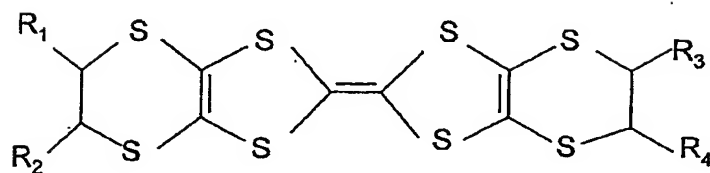


Fig. 14c

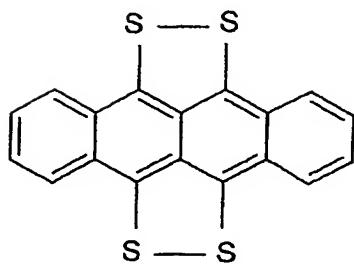


Fig. 14d

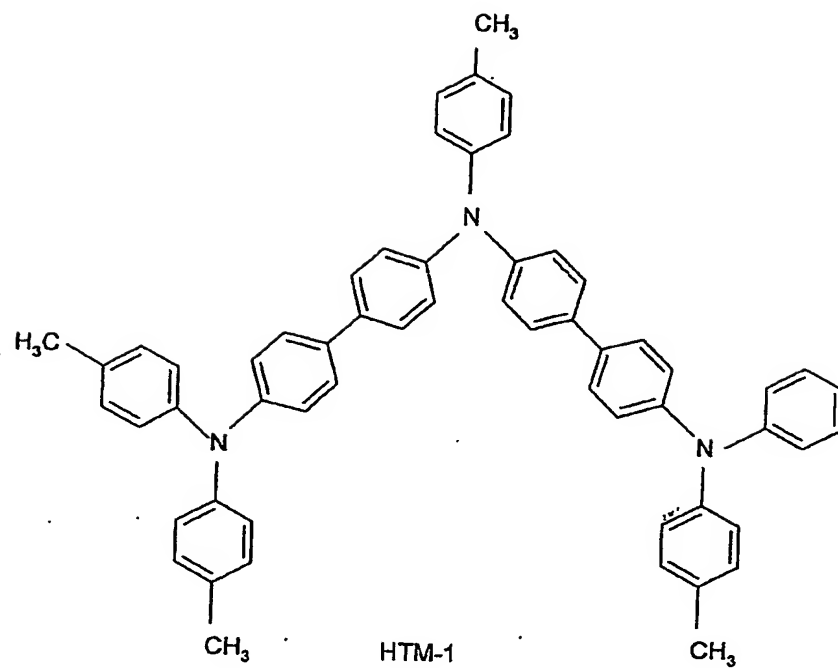


Fig. 15a

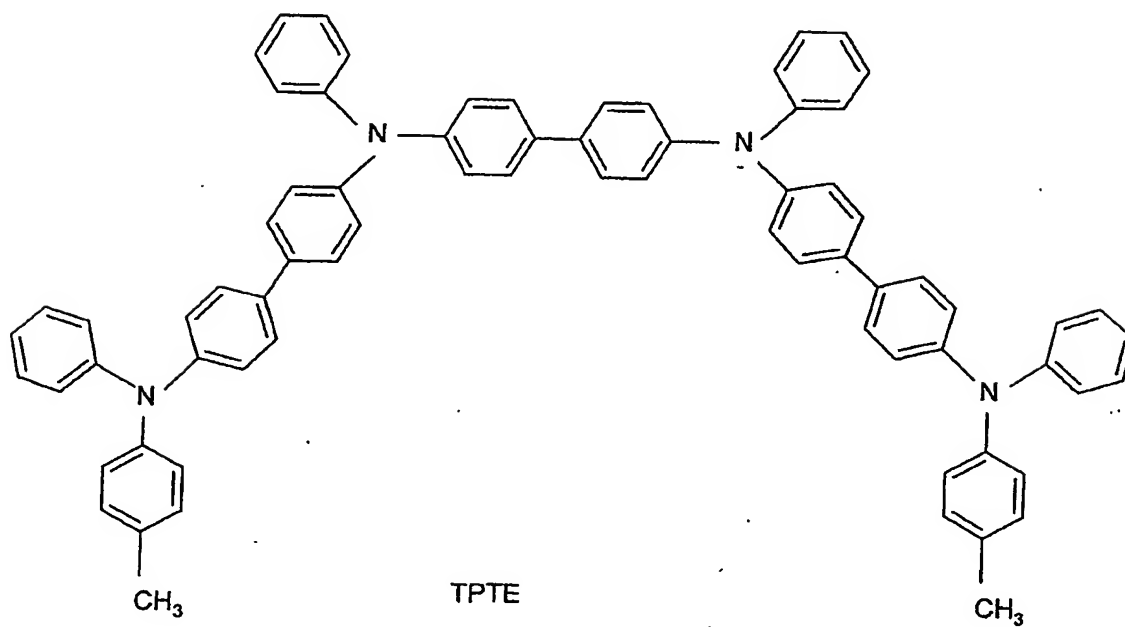
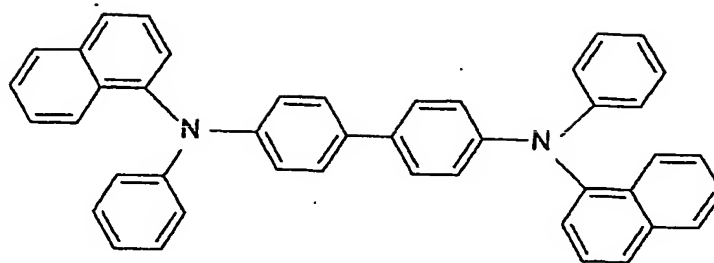
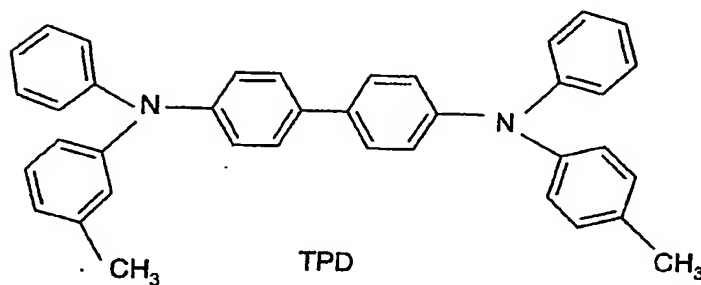


Fig. 15b



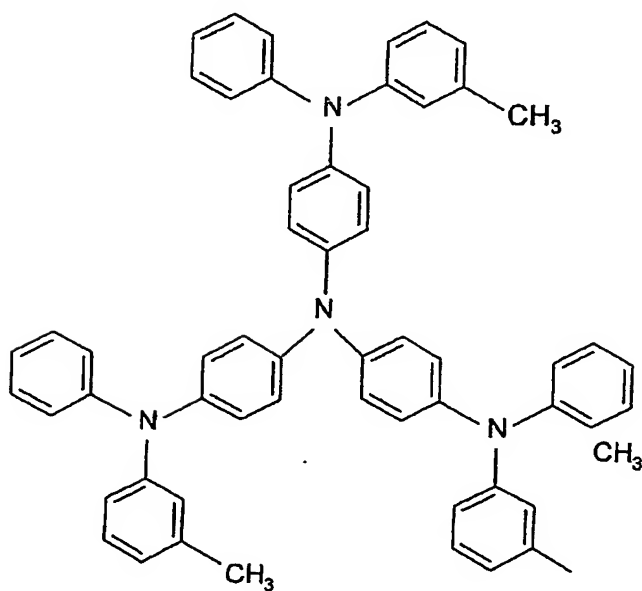
$\alpha$ -NPB

Fig. 16a



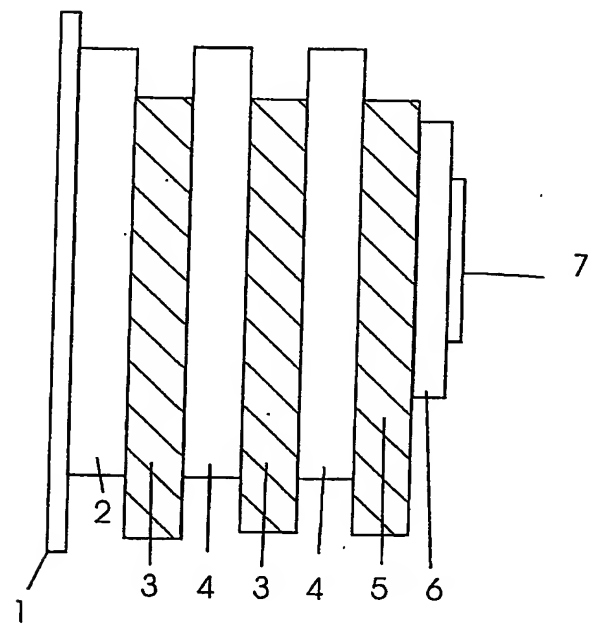
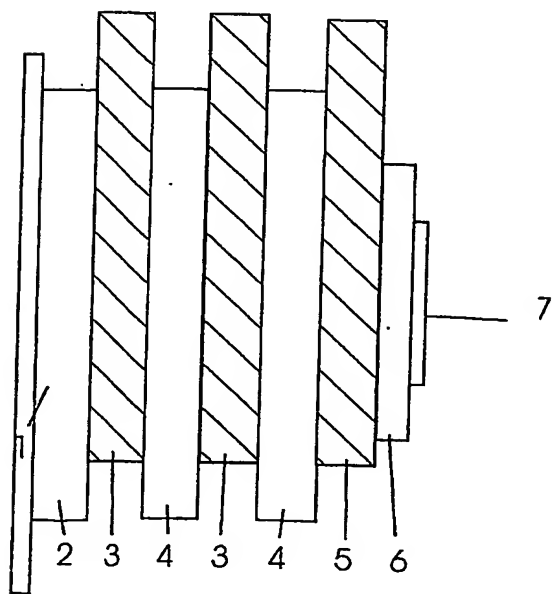
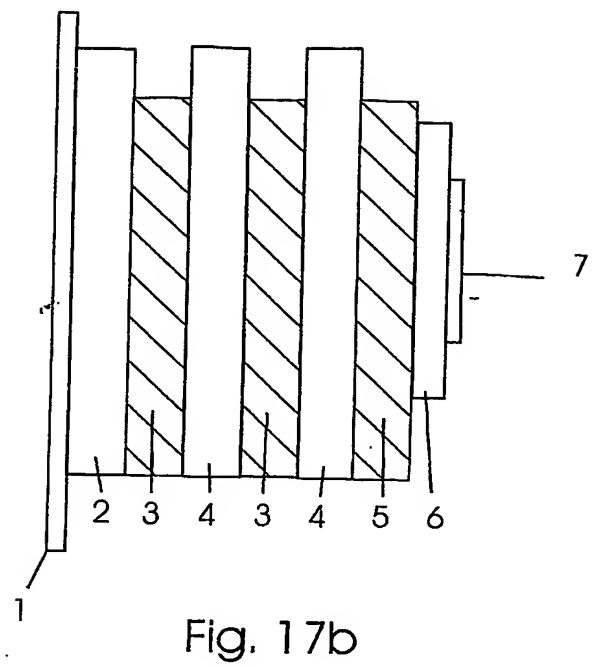
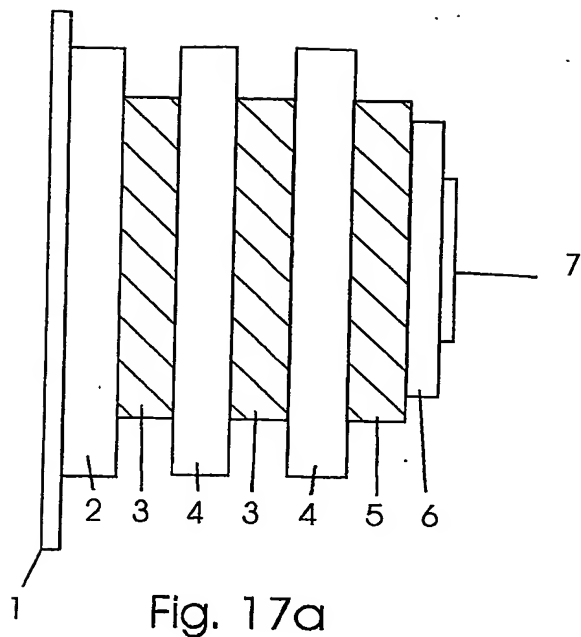
TPD

Fig. 16b



mTADATA

Fig. 16c





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